Ionic Contributions to Lattice Instabilities and Phonon Dispersion in La_2CuO_4

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We have applied the potential-induced breathing model, a nonempirical ionic model, to La_2CuO_4. The ionic model predicts the observed tetragonal-to-orthorhombic distortion, predicts a lower-symmetry ground state, and predicts a stable oxygen breathing mode. We find unstable phonon branches that we relate to phase transitions. Harmonically unstable double-well modes will couple to the charge density in the copper-oxide planes and possibly contribute to high-T_c superconductivity. This ionic coupling is not included in recent calculations.

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The new high-T_c oxide superconductors[1,2] display an unusual combination of ionic and metallic characteristics. Several theoretical studies of the electronic structures that concentrate on the band structure and metallic properties of these materials have now been performed.[3-7] Here we investigate the structural and lattice-dynamical properties of the nonmetallic material La_2CuO_4 upon which the 40-K superconductors are based.

The potential-induced breathing (PIB) model has shown success in the calculation of relative phase stability, structures, elasticity, and thermal equations of state in insulating oxides.[8-12] PIB is an *ab initio* description; no fitting to experiment is performed. The charge density for the PIB model of a crystal is given by overlapping, Watson-sphere stabilized ions. The total energy in the PIB model is calculated with a local-density formalism for the kinetic energy, as well as the exchange and correlation functionals, and is the sum of three parts: the self-energy of each ion, the overlap energy, and the Madelung energy for the overlapping ion charge density.

The PIB charge density is subtracted from the total self-consistent crystalline charge density for tetragonal La_2CuO_4 calculated with the linearized augmented plane-wave (LAPW) method[13] in order to examine the difference in the charge density from spherical ions (Fig. 1). The PIB charge density is that for the overlapping ions La^{3+}, O^{2-}, and sphericalized Cu^{2+}. The difference density is very small for the out-of-plane oxygen O_z. The differences at the La are due to orthogonalization of the oxygen tails to the La core states, small amounts of La f character, and/or static polarization. Major differences are found only in the copper-oxygen plane; charge moves *out* of the overlap regions in order to minimize the repulsive overlap energy. The copper shows a deficiency of charge, relative to spherical overlapping ions, in antibonding $d_{x^2-y^2}$-like states, and an excess of charge in nonbonding d_{z^2}-like states. The oxygen shows smaller differences than the copper, but charge similarly moves out of the overlap regions. There is a small bonding excess at the midpoints between the copper and the in-plane oxygen. The fact that these differences between LAPW and PIB charge densities are small illustrates the

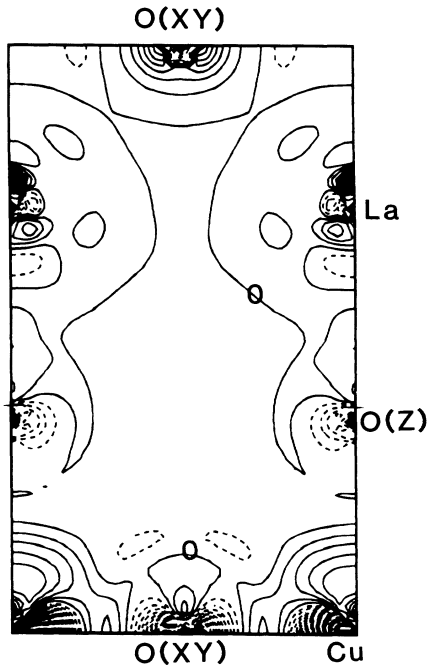

FIG. 1. Difference charge density in the (100) plane for tetragonal La_2CuO_4. The PIB overlapping-ion charge density is subtracted from the self-consistent LAPW charge density. The contour interval is 0.005 e/Bohr^3. The dashed contours are negative.

usefulness of ionic charge densities as reference models. The charge-density distortions that are apparent in the difference map are not readily apparent in the LAPW valence charge densities, because the differences are small relative to the total valence charge density. The charge density in the ionic picture primarily differs from the self-consistent charge density by nonspherical deformations associated with the open-shell character of the copper. This is not necessarily a discrepancy with the ionic characterization; PIB could be generalized to include nonspherical deformations. In any case, spherical ions with full ionic charges are appropriate for the O_z and the La.

Minimum-energy structures of La_2CuO_4 were calculated in the tetragonal and orthorhombic space groups and are compared with experiment[14,15] in Table I. PIB predicts distorted octahedra in the tetragonal structure, with a Cu-O_z distance of 2.34 Å and a Cu-O_{xy} distance of 2.00 Å, compared with experimental values of 2.41 and 1.89 Å. Thus the Jahn-Teller distortion, which is not included in PIB, is responsible for only about half of the distortion of the Cu octahedron. PIB predicts a tilting distortion that reduces the symmetry from tetragonal to orthorhombic, identical to what is observed experimentally.[16] In fact, PIB predicts a larger distortion than is observed experimentally. No other calculation, to our knowledge, predicts this distortion. The calculated volumes of both phases are overestimated; use of spherical ions puts too much charge in the overlap region (Fig. 1), which causes the calculated structure to expand. The tendency for the octahedra to tilt also increases since the tilting mode increases the Cu-O distances.

Frequencies were calculated from Γ to X for the calculated zero-pressure structures for tetragonal and orthorhombic La_2CuO_4 (Fig. 2) by the methods described in Ref. 10. This approach is appropriate for insulating La_2CuO_4, where metallic screening does not arise. For doped metallic samples, the LO and TO branches at Γ are expected to come together for wave vectors of the order of the inverse screening length. In the tetragonal structure, which is known to be stable only above 500 K, several branches are harmonically unstable; imaginary frequencies are represented here as negative numbers. The squares of imaginary frequencies represent the curvature of maxima in anharmonic, double-well potential surfaces. When the structure is allowed to relax to the orthorhombic structure, most of these unstable branches become stable. The remaining unstable branches indicate a monoclinic or lower-symmetry ground state, and evidence of such a low-temperature transformation has been observed.[17,18] Complete eigenvectors are given elsewhere.[19] Phonon frequencies were also calculated on a uniform mesh of 25 points in the irreducible wedge of the Brillouin zone for the orthorhombic structure to calculate the distribution moments for La_2CuO_4. Imaginary frequencies were not counted in the sums. The calculated moments with respect to $F(\omega)/\omega$, which are important for superconductivity, are $\omega_{\log}=136$, $\langle\omega\rangle=230$, and $\langle\omega^2\rangle^{1/2}=300$ cm^{-1}.

TABLE I. Minimum-energy structures for La_2CuO_4.

	Tetragonal *I4/mmm*		Orthorhombic *Abma*	
	PIB	Expt.[a]	PIB	Expt.[b]
V (Å^3)	99.19	94.88	205.76	189.76
c/a	3.01	3.49	2.14	2.43
b/a	(1.0)	(1.0)	1.016	1.008
La(X)	(0.0)	(0.0)	-0.023	0.007
La(Z)	0.366	0.362	0.350	0.362
O_{xy}(Z)	(0.0)	(0.0)	0.062	0.007
O_z(X)	(0.0)	(0.0)	-0.151	-0.031
O_z(Z)	0.193	0.182	0.183	0.187

[a] Reference 14. [b] Reference 15.

The most unstable modes are calculated to occur at the X point in tetragonal La_2CuO_4. The B_{1g} (X_2) mode at -366 cm^{-1} is a quasirotational mode in which the O_{xy} atoms move around the [001] axis. The next most unstable is the tilting mode ($B_{3g}=X_4$) that leads from the tetragonal structure to the *Abma* orthorhombic structure observed experimentally. Note that formulations that attribute the instability to Fermi-surface effects not only are physically unappealing (La_2CuO_4 is nonmetallic) but also do not obtain the observed orthorhombic distortion. For example, the calculations of Weber[5] incorrectly predict a freezing in of the oxygen breathing mode, which PIB predicts to be the highest vibrational frequency.

The most unstable mode calculated in the tetragonal structure is the rotational mode at the X point of the O_{xy} atoms around the [001] axis($B_{1g}=X_2$). The most unstable mode at the Γ point in the tetragonal phase is an infrared-active mode ($E_u=\Gamma_{5'}$) that involves sliding motions of the La and O_z in the x-y plane. In the orthorhombic structure these sliding motions, which have infrared-active B_{2u} ($\Gamma_{3'}$) symmetry at the zone center, become the most unstable, with a harmonic frequency of -185 cm^{-1}. However, the dispersion for this mode is extremely small [Fig. 2(b)]. Thus PIB predicts the instability to be very insensitive to the wave vector of the distortion. The dispersion along Γ to Z [$q=(001)$] is also negligible. The fluctuations are predicted to have little or no long-range order. Disorder for an infrared-active motion in the planes between the copper-oxygen planes would induce charge distortions in the metallic planes of the doped materials that may be important for superconductivity. Neutron-diffraction studies[16] indicate large-amplitude thermal ellipsoids for O_{xy}, O_z, and La in accordance with the modes that are unstable in the PIB model and in contradiction with unstable breathing-type motions predicted by Weber.[5]

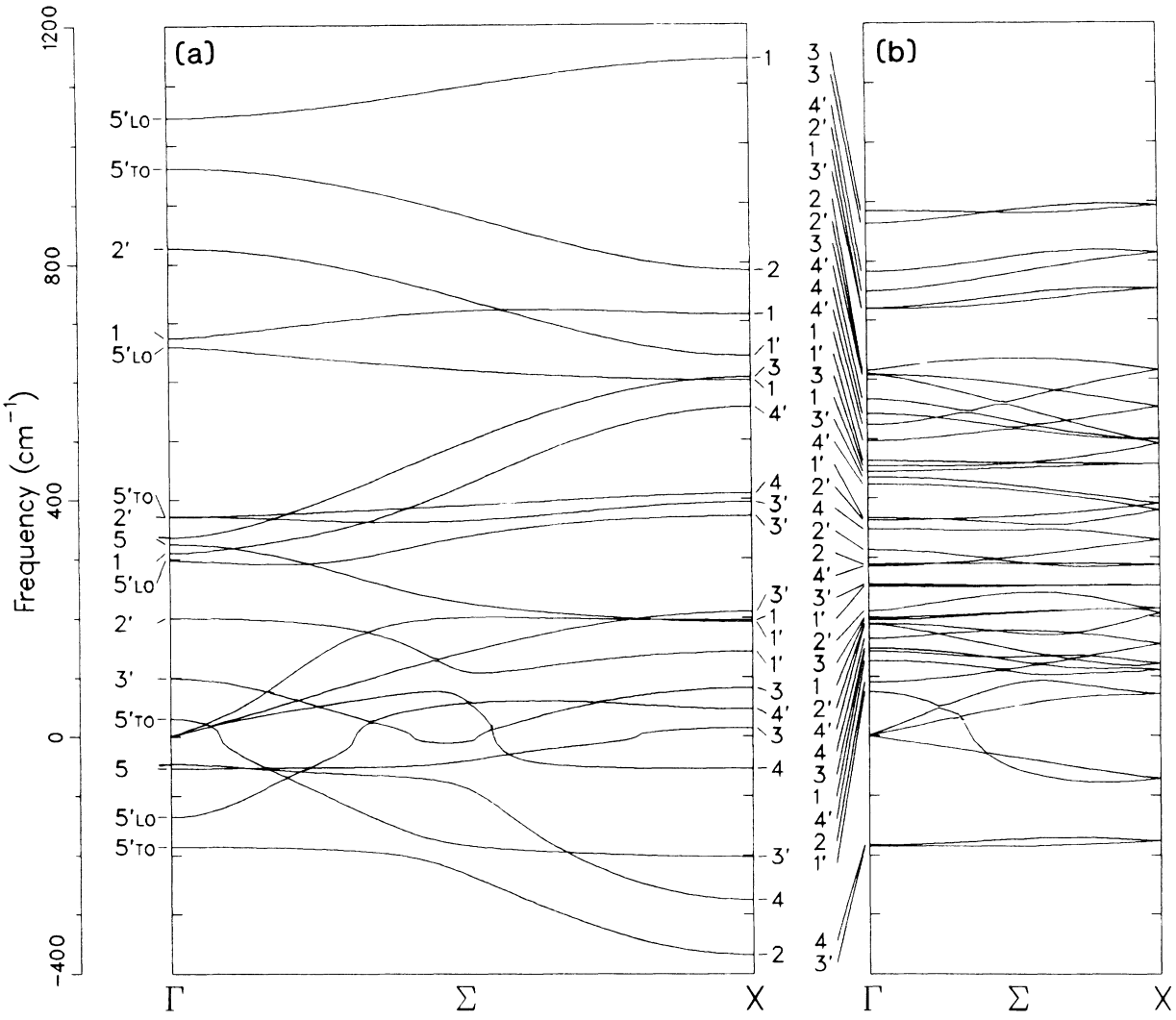

FIG. 2. (a) Calculated dispersion curves from Γ to X, $q=(110)$, for tetragonal La_2CuO_4. (b) Calculated dispersion curves from Γ to X, $q=(100)$, for orthorhombic *Abma* La_2CuO_4. The numbers indicate the symmetry labels.

Fu and Freeman[20] calculated a harmonic frequency of approximately 930 cm^{-1} for an oxygen breathing distortion in a two-dimensional slab of La_2CuO_4. Their result agrees fairly well with the PIB estimate of 1142 cm^{-1} in spite of their use of the metallic band structure which arises in a paramagnetic band calculation. It should also be noted that Fu and Freeman neglected the O_z motions as well as the three-dimensional crystallinity. PIB predicts the O_z motions to be about 25% of the O_{xy} motion for the breathing mode. The O_z motions are in phase with the O_{xy} motions; the O_z atoms move in towards a Cu as the O_{xy} atoms move in. Thus the frequency for the oxygen breathing mode in a slab is probably higher than that given by Fu and Freeman, closer to that predicted by PIB.

The zone-boundary breathing mode for the tetragonal structure folds into the zone center and mixes with the axial oxygen breathing mode in the orthorhombic structure; thus there are two zone-center mixed breathing modes in *Abma* La_2CuO_4 that are both Raman active. Renker *et al.*[21] find breathing modes at 500 and 750 cm^{-1}, compared with 445 and 885 cm^{-1} in PIB. Stavola, Cava, and Rietman[22] identify an infrared mode at 677 cm^{-1} as the folded oxygen breathing mode; however, this is impossible without some additional mechanism to mix the Raman- and infrared-active modes (local disorder, for example), since the breathing modes are purely Raman active in the orthorhombic structure. Bergeneau *et al.*[23] have measured phonon dispersion below 145 cm^{-1} along $(qq0)$ for a single crystal of La_2CuO_4 using inelastic neutron scattering. The hybridization of a low-frequency optic mode with a TA mode leading to a mode that drops in frequency towards the zone boundary is observed. They interpret this zone-boundary mode as

the octahedral tilting mode. Our calculations [Fig. 2(a)] give qualitatively the same picture.

It appears that a nonempirical ionic description can account for many of the features of La_2CuO_4 qualitatively and semiquantitatively. In particular, there is no need to invoke[24] many-body effects to account for the structural phase transition. Although our calculations are for nonmetallic La_2CuO_4, we are aware of no experimental evidence for significant differences between the lattice dynamics of insulating and conducting samples. Thus we expect our results to be relevant to high-T_c superconductors, and features of these oxides that are ionic in nature may give important contributions to superconductivity and high T_c's. The oxygen ion is fundamentally unstable; O^{2-} is not stable in the free state. Since the oxygen ion is stabilized by the crystal field, fluctuations in the field can lead to large charge deformations. Because of this coupling, ion motions that change the electrostatic field can move charge between oxygen and the copper, and the coupling may be significantly larger than calculated up to now.[5,6] Anharmonic double-well potentials for normal modes may give larger coupling than expected from harmonic phonons, and are, furthermore, less sensitive to the mass.[25] These interactions may help contribute to more than one coupling mechanism and may help boost the superconducting temperatures in copper-oxide superconductors.

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